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1 A procedural development for the analysis of $^{56/54}\text{Fe}$ and $^{57/54}\text{Fe}$ isotope
2 ratios with new generation IsoProbe MC-ICP-MS.

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4 Romain Guilbaud^{†,§,*}, Rob M Ellam^{†,§}, Ian B Butler^{†,§}, Vincent Gallagher[‡] and Kathleen
5 Keefe[‡]

6 [†]*School of Geosciences, University of Edinburgh, Edinburgh, UK*

7 [‡]*Scottish Universities Environmental Research Centre, East Kilbride, UK*

8 [§]*ECOSSE (Edinburgh Collaborative of Subsurface Science and*
9 *Engineering). A Joint Research Institute of the Edinburgh Research*
10 *Partnership in Engineering and Mathematics.*

11

12 *Email: R.Guilbaud@sms.ed.ac.uk

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14 We have developed a procedure for iron isotope analysis using a hexapole collision cell MC-
15 ICP-MS which is capable of Fe isotope ratio analysis using two different extraction modes.
16 Matrix effects were minimised and the signal-to-background ratio was maximised using high-
17 concentration samples (~ 5µg Fe) and introducing 1.8 mL/min Ar and 2 mL/min H₂ into the
18 collision cell to decrease polyatomic interferences. The use of large intensity on the faraday
19 cups considerably decreases the internal error of the ratios and ultimately, improves the
20 external precision of a run. Standard bracketing correction for mass bias was possible when
21 using hard extraction. Mass bias in soft extraction mode seems to show temporal instability
22 that makes the standard bracketing inappropriate. The hexapole rf amplitude was decreased to
23 50 % to further decrease polyatomic interferences and promote the transmission of iron range
24 masses. We routinely measure Fe isotopes with a precision of ± 0.05 ‰ and ± 0.12 ‰ (2σ)
25 for δ⁵⁶Fe and δ⁵⁷Fe respectively.

26

27 Keywords: Fe isotopes, IsoProbe, MC-ICP-MS, hard extraction, soft extraction.

28

29 **Introduction**

30 The field of transition metal geochemistry has seen increasing development throughout the
31 last twenty years and particularly since the introduction of multi-collector inductively coupled
32 mass spectrometry MC-ICP-MS.¹⁻³ Iron is the ninth most abundant element in the universe⁴
33 with four stable isotopes: ⁵⁴Fe (5.845 %), ⁵⁶Fe (91.754 %), ⁵⁷Fe (2.1191 %) and ⁵⁸Fe (0.2819
34 %).⁵ The first attempts to measure Fe isotopic ratios began 60 years ago.⁶ Thermal ionisation
35 mass spectrometry, TIMS, has been applied to iron since the 1980s (*e.g.* Walczyk⁷; Gotz &

36 Heumann⁸; Bullen & McMahon⁹) with a precision down to $\pm 0.6 \text{ ‰}$ (2σ).^{10,11} However, TIMS
37 was challenging because of the large spectrometer mass discrimination (mass fractionation)
38 and the low ionisation efficiency for Fe analysis (the first ionisation potential is 7.870 eV).
39 MC-ICP-MS, characterised by a higher ionisation efficiency and a very stable mass bias
40 (although larger than TIMS, from 3 to 6%/amu), has become the technique of choice since its
41 development in the 1990s.

42 Fe isotope analysis has seen growing attention in the Earth and environmental sciences
43 for its potential use for tracing biogeochemical cycles. Because of their relative small mass
44 difference, it was generally agreed that Fe isotopes could fractionate in nature solely via
45 biological assimilation and preferential uptake by organisms. Recent studies have now
46 indicated that Fe isotope fractionation can also occur abiotically in low temperature aqueous
47 systems¹²⁻¹⁴ and at high temperature.¹⁶⁻¹⁸

48 The principal difficulty in measuring precisely and accurately Fe isotope ratios is the
49 removal of polyatomic and atomic mass interferences induced by the Ar plasma. Additional
50 interferences can be due to sample matrix. Among these interferences are $^{40}\text{Ar}^{14}\text{N}^+$ and $^{54}\text{Cr}^+$
51 on $^{54}\text{Fe}^+$, $^{40}\text{Ar}^{16}\text{O}^+$ on $^{56}\text{Fe}^+$, $^{40}\text{Ar}^{16}\text{OH}^+$ on $^{57}\text{Fe}^+$, and $^{40}\text{Ar}^{18}\text{O}^+$ and $^{58}\text{Ni}^+$ on $^{58}\text{Fe}^+$. Various
52 strategies have been developed to reduce interferences created by the Ar plasma: i) sample
53 desolvation and the use of high-concentration samples,¹⁹⁻²⁴ ii) cold plasma,^{25,26} iii) collision
54 cells²⁷⁻³⁰ and iv) high resolution multi-collection.³¹⁻³³

55 In this contribution, we detail a procedure developed for the analysis of Fe isotope ratios
56 on a new generation GV Instruments (formerly Micromass) IsoProbe-P MC-ICP-MS at the
57 Scottish Universities Environmental Research Centre (East Kilbride, UK). This instrument
58 enables us to conduct the ion extraction in two modes: the hard and the soft extraction modes.
59 Although Fe isotope ratios have been published using both extraction modes,^{29,33} no study
60 compares the effect of each mode on the external precision and the overall stability of the
61 measurement of Fe isotope ratios. Therefore, we have inspected the effects of extraction
62 voltage, sample uptake rate, the hexapole potential difference and the collision gases on the
63 overall stability of Fe isotope analysis.

64

65 **Analytical materials and methods**

66 **Samples and standards preparation**

67 All samples used in this study are part of an experimental investigation of iron sulphide
68 geochemistry; therefore all samples are synthetic iron sulphide species (FeS and FeS_2) and
69 $\text{Fe(II)}_{\text{aq}}$. Solutions were prepared using 18.2 M Ω cm deionised water. Fe and S source reagents
70 were analytical grade $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ (Sigma AldrichTM) respectively.
71 HNO_3 and HCl were twice distilled, HF was once distilled. Once experimentally synthesised,

72 solid samples were separated and dissolved in 6 M HCl or concentrated HNO₃ depending on
73 the mineral, taken to dryness and re-dissolved in 5 % v/v HNO₃. The solution was then
74 effectively Fe(III) in nitric acid (S being removed as H₂S gas), and thus no column separation
75 chemistry was performed on our samples.

76 IRMM-014 (IRMM™) was used as a bracketing reference standard for the δ calculation,
77 i.e. before and after each sample. The isotopic concentrations of IRMM-14 are in percent,
78 5.845 ± 0.023 (2σ) for ⁵⁴Fe, 91.754 ± 0.024 for ⁵⁶Fe, 2.1192 ± 0.0065 for ⁵⁷Fe, and $0.2818 \pm$
79 0.0027 for ⁵⁸Fe.⁵ These concentrations are close to the natural Fe isotope distribution. IRMM-
80 014 Fe wire was dissolved on a hot plate in 5 % v/v HNO₃. Our external standard for
81 determination of precision was prepared from a 1 g/L Fe solution (J.T Baker™).

82

83 **Mass Spectrometry**

84 Analyses were performed the GV Instruments (formerly Micromass) IsoProbe MC-ICP-MS.
85 Table 1 summarises the routine instrumental settings for Fe isotope analysis. Mass 54, 56, 57
86 and 58 were measured simultaneously on the multi-collection faraday cups in a static mode
87 (Fig. 1). Cr interferences were monitored on mass 52 for further correction on mass 54.
88 However, since our samples were experimentally synthesised, Cr contributions were never
89 detected. Ni interferences on mass 58 should be monitored on mass 60, but on our instrument,
90 it was physically not possible to align mass 60 on any cup, the range of masses being so large.
91 In the case of this study, that is not a problem since only ^{56/54}Fe and ^{57/54}Fe were required.
92 Faraday cups were calibrated and displayed linear response over a 1 ppm to 8 ppm range.
93 Typical response was 0.6 to 2 V/ppm and our sample solutions were 3 to 10 ppm Fe in 5% v/v
94 HNO₃ (samples and/or standards) to obtain ~ 0.35 V on mass 54, ~ 6 V on mass 56, ~ 0.14 V
95 on mass 57 and 0.024 V on mass 58.

96 Solutions were introduced into an ApexQ (Elemental Scientific™) inlet system which
97 comprises a PFA nebuliser and a cyclonic desolvating spray chamber. The ApexQ was
98 operated with Ar sweep gas and without the addition of N₂ to avoid further formation of
99 ⁴⁰Ar¹⁴N⁺ on mass 54. The condenser cooling temperature was set at 2°C and the temperature
100 of the spray chamber at 100°C. Both 50 μ L/min and 100 μ L/min uptake rates were
101 investigated.

102 The instrument high tension was set at -6000 V. Ion extraction from the source into the
103 mass analyser can be run in two modes, called hard and soft extraction. We routinely run our
104 samples using the hard extraction mode at -250V but both approaches were investigated and
105 the results will be described later.

106 The IsoProbe incorporates a hexapole to the standard MC-ICP-MS instrumentation -
107 between the cones and the optics region - in order to reduce the ions' energy spread from ~

108 30eV to ~ 1eV, allowing a single focusing magnetic sector analyser. Ions are transmitted with
 109 a mass resolution ~ 500 $\Delta m/m$ which is not sufficient to separate Fe peaks from polyatomic
 110 interferences. Fe peaks can be separated from molecular interference peaks with a resolving
 111 power of ~3000³⁴ and flat peaks can be preserved with resolving power of ~9000 (High
 112 resolution³¹). To reduce or remove polyatomic interferences, the hexapole can be used as a
 113 reaction cell. The introduction of collision gases (Ar and H₂) into the hexapole induces a
 114 series of ion-molecule reactions leading to the decrease of argides, oxides and hydrides in the
 115 ion beam. 1.8 mL/min Ar and 2 mL/min H₂ were introduced into the hexapole collision cell to
 116 completely remove ⁴⁰Ar¹⁴N⁺ and ⁴⁰Ar¹⁶OH⁺ on mass 54 and mass 57 respectively, and to
 117 decrease ⁴⁰Ar¹⁶O⁺ on mass 56 to 0.006 V which represents 0.1 % of the Fe peak. **After**
 118 **subtraction, interference contributions were smaller than the analytical precision.** There was
 119 no peak on mass 55 suggesting that FeH⁺ did not form even at high Fe concentrations.

120 On-peak-zero correction was measured on a 5% v/v HNO₃ solution prior to each Fe
 121 solution (samples or standards). Data collection consisted of 5 blocks of 20 5 x 1s
 122 integrations, followed by a 4 min rinse in 5% v/v HNO₃ + 2% v/v HF. Mass bias was
 123 corrected using IRMM-014 as a bracketing standard (Eq. 1 and 2). The external standard was
 124 measured five times before the run of samples. During the run, one external standard was
 125 measured after every four samples.

126 Data are reported in conventional fashion using per mil δ notation, $\delta^{56}\text{Fe}$ and $\delta^{57}\text{Fe}$,
 127 defined as (1) and (2):

$$128 \quad \delta^{56}\text{Fe} = \left(\frac{(^{56}\text{Fe}/^{54}\text{Fe})_{\text{sample}}}{(^{56}\text{Fe}/^{54}\text{Fe})_{\text{std}}} - 1 \right) \times 10^3 \quad (1)$$

$$129 \quad \delta^{57}\text{Fe} = \left(\frac{(^{57}\text{Fe}/^{54}\text{Fe})_{\text{sample}}}{(^{57}\text{Fe}/^{54}\text{Fe})_{\text{std}}} - 1 \right) \times 10^3 \quad (2)$$

130

131 where *std* is the reference material *IRMM-014* (IRMMTM).

132

133 **Procedural development**

134 **Theoretical and observed errors**

135 The external precision on $\delta^{56}\text{Fe}$ and $\delta^{57}\text{Fe}$ is given by the 95% reproducibility (2 σ standard
 136 deviation) of the δ external standard repeated at least twelve times. The external precision
 137 should approximate the internal error of each individual ratio (2se) which is the 95%
 138 confidence limits on the mean ratio. Ludwig³⁵ showed that the internal error is the result of a

139 combination of shot noise (error on the measurement of ions) and Johnson noise (from the
 140 Faraday amplifier). The overall theoretical error on a measured Fe isotope ratio is given by
 141 Eq. 3:

$$142 \quad \%2se = 2 \times \frac{\frac{^{56}\text{Fe}}{^{54}\text{Fe}} \sqrt{\underbrace{\left(\frac{1}{V_{^{56}\text{Fe}}} + \frac{1}{V_{^{54}\text{Fe}}} \right) \times \left(\frac{1.6 \times 10^{-8}}{t} \right)}_{\text{Shot-noise}} + \underbrace{2 \times 0.000014^2 \times \left(\frac{1}{V_{^{56}\text{Fe}}^2} + \frac{1}{V_{^{54}\text{Fe}}^2} \right)}_{\text{Faraday-noise}}}}{\sqrt{N}} \quad (3)$$

143 where V is the voltage on the peak and t is the time of the measurement (10 min).

144 It is intuitive to think that the larger the internal errors of the mean are, the larger the
 145 external error on the overall run should be. However, it is not possible to demonstrate this
 146 mathematically because in the 2sd calculation we do not take in account the internal error of
 147 each individual δ value. In Fig. 2A, we plot the mean 2se of the ratios during several run
 148 times against the external precision of the run. We demonstrated graphically that for the
 149 external precision to be $\leq \pm 0.1 \text{ ‰}$ and $\leq \pm 0.15 \text{ ‰}$ (2σ) for $\delta^{56}\text{Fe}$ and $\delta^{57}\text{Fe}$, the internal error
 150 over a run time should not exceed $\sim 0.0018\%$ and $\sim 0.0025\%$ for $^{56/54}\text{Fe}$ and $^{57/54}\text{Fe}$
 151 respectively. Rearranging Eq. 4 demonstrates that the voltage on ^{56}Fe must be $> 4\text{V}$ to
 152 produce such small errors, justifying the use of high-concentration samples. Collecting $\sim 6\text{V}$
 153 on mass 56 enables us to decrease the internal error down to 0.0013% (Fig. 2B). We could
 154 measure accurately Fe isotope ratios with an internal error (%2se) systematically $< 0.0020 \text{ ‰}$
 155 and $< 0.0030 \text{ ‰}$ for $^{56/54}\text{Fe}$ and $^{57/54}\text{Fe}$ respectively. The precision of our measurements was \pm
 156 0.05 ‰ and $\pm 0.12 \text{ ‰}$ (2σ) for $\delta^{56}\text{Fe}$ and $\delta^{57}\text{Fe}$ respectively.

157

158 **Matrix effects and sample uptake**

159 The reduction of interferences and their effects is crucial for precise and accurate
 160 measurements. This was achieved by the use of collision gases (see below) and maximising
 161 the source-to-background ratio by introduction of high-concentration samples (up to 10 ppm).
 162 Sample matrix is a potential source of interferences, with direct effects on the overall
 163 reproducibility. We compared bracketing our external standard (Fe solution from
 164 J.T.Baker™) with bracketing IRMM-014 itself. The Baker solution, which is essentially an
 165 iron sulphate solution led to a reproducibility of $\pm 0.05 \text{ ‰}$ and $\pm 0.12 \text{ ‰}$ (2σ) for $\delta^{56}\text{Fe}$ and
 166 $\delta^{57}\text{Fe}$ respectively. IRMM-014 solution, which is dissolved Fe in HNO_3 , bracketed with itself,
 167 led to a precision as good as $\pm 0.05 \text{ ‰}$ and $\pm 0.05 \text{ ‰}$ (2σ) for $\delta^{56}\text{Fe}$ and $\delta^{57}\text{Fe}$ respectively.

168 The uptake rate is determined by the diameter of the auto-sampler capillary. Both 50
 169 $\mu\text{L}/\text{min}$ and 100 $\mu\text{L}/\text{min}$ uptake rates were used. Twice as much material was consumed using
 170 the 100 $\mu\text{L}/\text{min}$ rate, doubling the sensitivity. However, the stability of a measurement was
 171 systematically decreased as well, leading to internal errors $> 0.0050\%$ and $> 0.0100\%$ for

172 $^{56/54}\text{Fe}$ and $^{57/54}\text{Fe}$ respectively. As a result, the measured Fe isotope ratios which are the mean
173 of the 100 integrations were not reproducible within an acceptable precision. We suspect that
174 this uptake rate was too high for the ApexQ inlet system to quantitatively dissolve the sample,
175 leading to inconsistent variations in the signal.

176 We examined the effect of the Fe concentration matching between the samples and the
177 reference standard IRMM-014 on the measured isotopic ratios. True ratios are obtained when
178 both the sample and the standard have the same concentration (Fig. 3). The effect is more
179 dramatic for $[\text{Fe}]_{\text{sample}} < [\text{Fe}]_{\text{std}}$, as suggested by other authors.^{22,36} We suspect that in this
180 region, Fe concentration is small relative to the interferences and therefore the peaks are
181 committed to variations in interference production from the plasma. The deviation from linear
182 response is thus due to plasma behaviour and not detector non-linearity over that range.

183

184 **Extraction mode: hard versus soft extraction**

185 Both hard and soft extraction modes have been used in laboratories for the analysis of Fe
186 isotopes.^{29,30,37,38} The hard extraction mode applies a strong negative voltage to the cones
187 (generally $\sim -600\text{V}$), while the soft extraction mode applies a small positive voltage to the
188 cones (0 to 20V). The soft extraction mode has been available only on new generations of the
189 IsoProbe, and has seen increasing interest since it considerably reduces molecular
190 interferences and memory effects.²⁹ We investigated the stability of the measurement during
191 100 integrations of the analysis in both hard and soft extraction (Fig. 4). In hard extraction,
192 internal errors (2se) produced on the ratios during 100 integrations (~ 10 min) are
193 systematically less than 0.0020% and 0.0040% for $^{56/54}\text{Fe}$ and $^{57/54}\text{Fe}$, while in soft extraction,
194 internal errors are 0.0060% and 0.0100% for $^{56/54}\text{Fe}$ and $^{57/54}\text{Fe}$ respectively. In all the
195 applications we have utilised soft extraction, we observe increased mass bias but this is not
196 necessarily detrimental if mass bias is internally corrected. However, for stable isotope
197 measurements of iron we need to make an external mass bias correction by reference to
198 bracketing standards. In soft extraction mode there is an increased time-dependent mass bias
199 instability, even over timescales of a few minutes, compared to the hard extraction mode. As a
200 result, a simple standard bracketing correction was not sufficient and the overall precision on
201 long term runs was always $> \pm 0.2 \text{ ‰}$ and $> \pm 0.6 \text{ ‰}$ (2σ) for $\delta^{56}\text{Fe}$ and $\delta^{57}\text{Fe}$ respectively.
202 We suspect that small voltage fluctuations in soft extraction mode have a more dramatic
203 effect on mass bias than in hard extraction considering their voltage range (0 to 20V versus 0 to
204 to -1500V for soft and hard extraction respectively). Thirlwall and Anczkiewicz³⁹ did a
205 comparative study for Hf, Nd and Pb isotopes using MC-ICP-MS and TIMS. They showed
206 that for Nd isotope ratios, hard extraction produced a larger mass bias than soft extraction.
207 This suggests that plasma chemistry and extraction voltage are not entirely comprehended yet.

208 Although hard extraction is usually operated at a cone voltage of $\sim -600\text{V}$ or higher to
209 maximise sensitivity, reducing the extraction potential to $\sim -250\text{ V}$ was a key for successful
210 Fe isotope measurements. At this voltage, molecular interferences on mass 52 are entirely
211 removed, and transmission of masses 54, 56 and 57 is optimised. The instrumental mass bias
212 is very stable and thus the standard bracketing technique is suitable.

213

214 **1. Hexapole tuning**

215 Hexapole tuning, i.e the rf amplitude (referred by some authors as Digital to analogue
216 convertor settings, or D.A.C settings) and the introduction of collision gases plays a dominant
217 role in optimising the transmission of ions. The IsoProbe collision cell can be used with two
218 hexapole rf generator devices ($6\text{M}\Omega$ or $9\text{M}\Omega$), the $9\text{ M}\Omega$ one being designed for measuring
219 low mass elements. Reducing the rf amplitude to $\sim 50\%$ enhances the transmission of low
220 masses. In the literature, reported rf amplitudes vary from 40% to 60% .^{29,30} The removal or
221 reduction of $^{40}\text{Ar}^{14}\text{N}^+$ and $^{40}\text{Ar}^{16}\text{O}^+$, $^{40}\text{Ar}^{16}\text{OH}^+$, $^{40}\text{Ar}^{18}\text{O}^+$ and FeH^+ interferences was achieved
222 by the introduction of collision gases (Ar and H_2) into the hexapole collision cell.^{27-29,34,40}
223 Arnold *et al.*⁴⁰ studied the mechanisms of polyatomic interferences removal and the behaviour
224 of $^{40}\text{Ar}^{16}\text{O}^+$, $^{40}\text{Ar}^{16}\text{OH}^+$ when varying Ar: H_2 ratios, flow rates, and the rf amplitude of the
225 hexapole. In our routine, the rf amplitude was set at 50% which decreases $^{40}\text{Ar}^{16}\text{OH}^+$, as
226 Arnold *et al.*⁴⁰ reported. Introducing 1.8 mL/min Ar into the hexapole removed completely
227 ArN^+ interference on mass 54. We thus investigated the effect of different H_2 flow rates on
228 the polyatomic interferences in a blank solution (Fig. 5). Introduction of H_2 has larger effects
229 on ArOH^+ (mass 57) than on ArO^+ (mass 56). ArOH^+ interferences were completely removed
230 with a H_2 flow rate of 2 mL/min .

231

232 **Fe isotope analysis of synthesised iron-sulfide minerals**

233 The procedure described above was applied to the analysis of synthetic iron sulphide species
234 and $\text{Fe(II)}_{\text{aq}}$. Samples were standard bracketed with IRMM-014 and the precision was given
235 by the external standard J.T.Baker Fe solution ($\delta^{56}\text{Fe} = -0.23 \pm 0.05\text{ ‰}$ and $\delta^{57}\text{Fe} -0.35 \pm 0.12$
236 ‰ , Fig. 6). Marechal *et al.*⁴¹ demonstrated that Zn mass bias on their VG Plasma 54
237 instrument was best fitted with an exponential law. In the case of Fe, the expected mass bias
238 slopes obtained with the power and the exponential laws are given respectively by Eq. 4 &
239 Eq. 5⁴²:

240

$$241 \quad \text{slope}_{57/54}^{57/54} = \frac{M_{57\text{Fe}} - M_{54\text{Fe}}}{M_{56\text{Fe}} - M_{54\text{Fe}}} = 1.501 \quad (4)$$

242
$$\text{slope}_{56/54}^{57/54} = \frac{\ln(M_{57\text{Fe}} / M_{54\text{Fe}})}{\ln(M_{56\text{Fe}} / M_{54\text{Fe}})} = 1.488 \quad (5)$$

243 where M is the atomic mass of the nuclide.

244 Our raw measurements all plot on the same mass fractionation line in a $\ln(^{57}\text{Fe}/^{54}\text{Fe})$
245 versus $\ln(^{56}\text{Fe}/^{54}\text{Fe})$ graph (Fig. 7), with a slope of 1.549 ± 0.003 which is consistent with Fe
246 isotope mass difference. When standard-bracketing corrected, our data ($\delta^{56}\text{Fe}$ and $\delta^{57}\text{Fe}$) plot
247 on the terrestrial mass fractionation line with a slope of 1.52 ± 0.02 (Fig. 8). Our experimental
248 work on synthesised FeS and FeS₂ from Fe(II)_{aq} shows large Fe isotope fractionations. These
249 results are preliminary and further experimental data are needed.

250

251 Conclusion

252 We have developed a procedure for the analysis of $^{56}\text{Fe}/^{54}\text{Fe}$ and $^{57}\text{Fe}/^{54}\text{Fe}$ ratios on a
253 hexapole collision cell MC-ICP-MS with a precision of ± 0.05 ‰ and ± 0.12 ‰ (2σ) for $\delta^{56}\text{Fe}$
254 and $\delta^{57}\text{Fe}$ respectively. This precision was achieved maximising the signal-to-background
255 ratio by using high-concentration samples (3 to 10 ppm) and introducing Ar and H₂ gases into
256 the hexapole collision cell. On our instrument, precise measurements are more readily
257 achieved using hard extraction, although in this mode the ArO⁺ interference at mass 56 was
258 not entirely removed. However, in hard extraction mode the instrument showed relatively
259 stable mass bias characteristics that allow the phenomenon to be corrected by sample-standard
260 bracketing. In soft extraction mode we observed temporal instability in mass bias to the
261 extent that sample-standard bracketing does not provide a reliable mass bias correction.

262

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 343

344 **List of tables:**

345 **Table 1:** IsoProbe settings. Tuning parameters are followed by an asterisk.

346 **Figure captions:**

347 **Figure 1:** alignment of the cups for simultaneous measurements of masses 52, 54, 56, 57 and
 348 58.

349 **Figure 2:** A: Empirical relationship between the mean of 2se during one set of measurement
 350 and the overall external precision of the run. B: Influence of the peak intensity (mass 56) on
 351 the theoretical error of the ratio $^{56/54}\text{Fe}$.

352 **Figure 3:** Concentration matching between samples and bracketing standards. Data plot on a
 353 mass fractionation line when both standards and samples have the same concentration.

354 **Figure 4:** Comparison of soft and hard extraction modes. A: variations of the measured ratio
 355 with time (100 integrations ~ 10 min). B: Mass bias associated with time (same data as A). C:
 356 Resulting fractionation lines on a long sample run.

357 **Figure 5:** A: Influence of the H₂ flow rate on polyatomic interferences. Ar flow rate is set at
 358 1.8 mL/min. B: Resulting Fe isotope spectrum after the decrease of the interferences.

359 **Figure 6:** External precision given by the reproducibility of the measurement of a standard.

360 **Figure 7:** log-log plot of the row data. Error bars are included in the data point.

361 **Figure 8:** plot of $\delta^{57}\text{Fe}$ versus $\delta^{56}\text{Fe}$ for iron sulphide species. Error bars are given by the
 362 reproducibility 2 SD of the external standard.

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